

# CEMENT AND LIME MANUFACTURE

VOL. XXV. No. 6

NOVEMBER 1952

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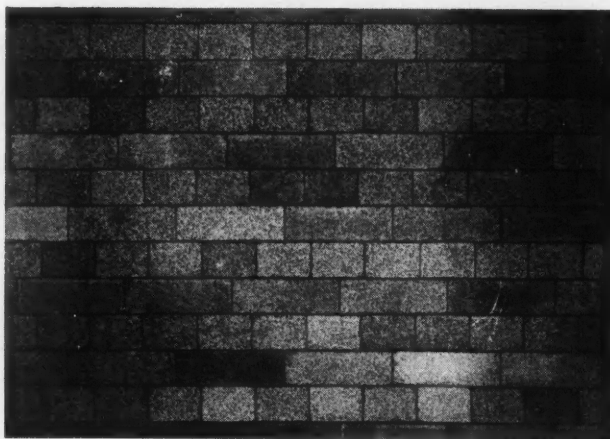
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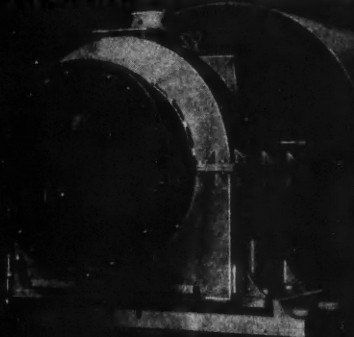
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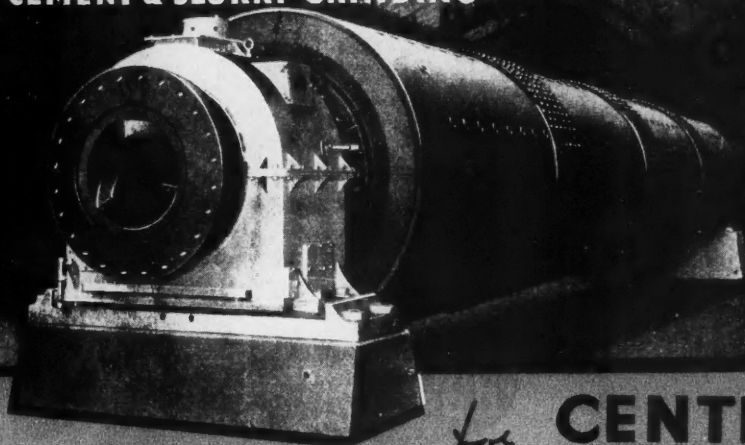
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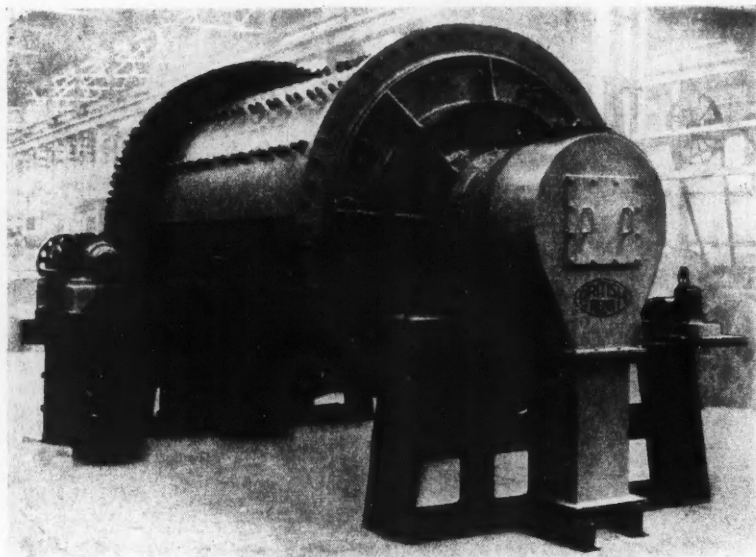
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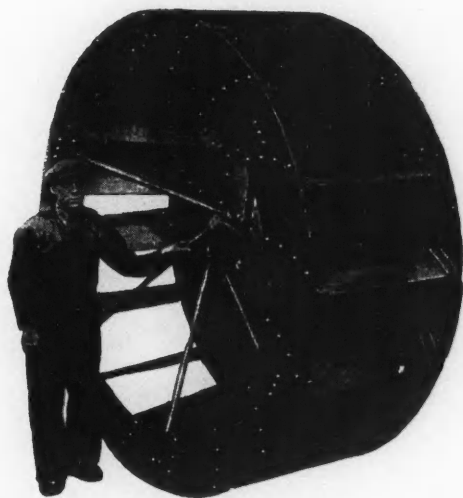
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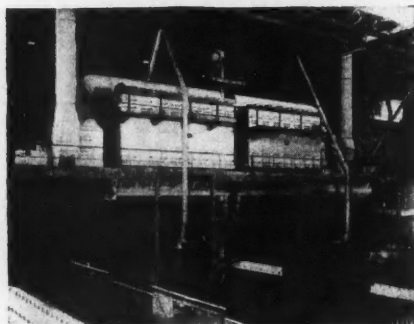
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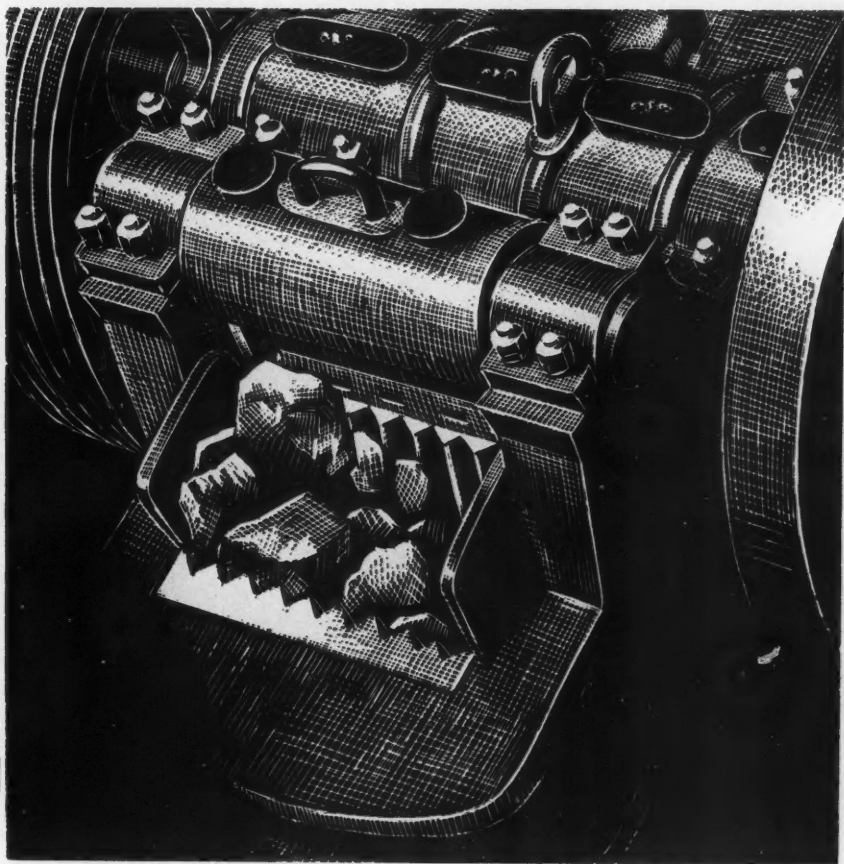
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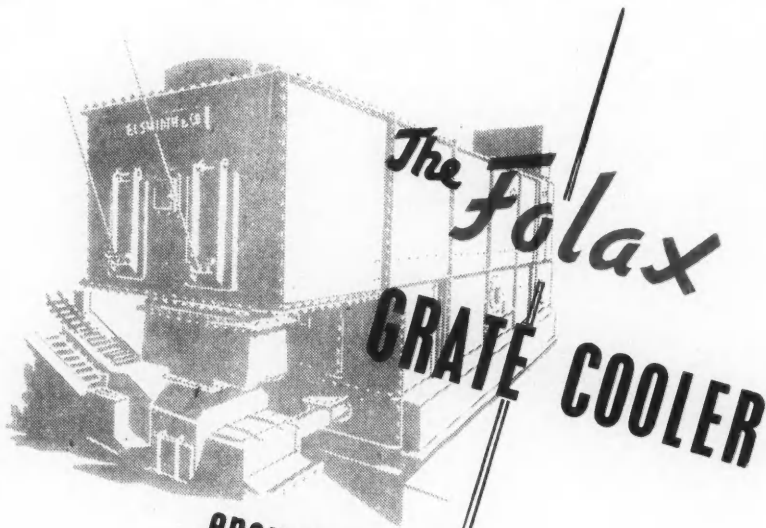
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TELEPHONE: WHITEHALL 4581.  
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CONCRETIUS, PARL, LONDON.

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## Symposium on the Chemistry of Cement.

The third International Symposium on the Chemistry of Cement was held in London in September last under the auspices of the Cement & Concrete Association. In the following abstracts are given of some of the papers. The complete papers are to be published in book form by the Association at 52 Grosvenor Gardens, London, S.W.1.

### The Structures of Cement Hydration Compounds.

By PROFESSOR J. D. BERNAL (Birkbeck College, London University).—Describes a study of hydrated calcium silicate compounds produced by hydration or precipitation methods under ordinary and hydrothermal conditions. Phases have been identified by X-ray methods making use of comparisons between synthetic products and natural minerals. The cell dimensions have been partially or completely determined for ten of these phases. The forms of hydrated calcium silicate stable at low temperatures have been shown to be two related types of structures of composition  $C_{1-1.5}SH_{2.5-1.6}$  and  $C_2SH_{4.2}$ . These occur in the form of extremely thin fibrous crystals, similar to those found in gels, and this may be related to the setting properties of cement. Evidence for the presence of these compounds has been found in pastes of hydrated tricalcium silicate and in a sand-lime brick. The first compound has been identified with the mineral riversideite. The structures of these compounds show the presence of a short fibre repeat unit of 3.65 Å, common to a number of other hydrated silicates, which is thought to imply the existence of silicate tetrahedra joined by hydrogen bonds. They also show a layer structure, the spacing of which varies on loss of water between 14 and 9 Å in a way similar to the clay minerals and which may be connected with the shrinking properties of concretes.

### Studies of the Constitution of Portland Cement Clinker.

By DR. R. H. BOGUE (Portland Cement Association Fellowship, National Bureau of Standards, Washington).—In this paper the principles for the repre-



sensation of multi-component systems on plane surfaces or solid models are discussed. Several devices are described by which geometrical limitations are by-passed and useful data obtained. These include the following of boundary curves by various means. A method for separating the liquid from the solid phases in the charge in the furnace is described. Mathematical means for establishing the relationships between the primary and subordinate systems are pointed out as a method for removing the limitations due to geometrical dimensions. These developments, together with improved equipment and methods, enable multi-component systems to be explored with assurance of useful results.

### **Developments in the Design and Construction of Concrete Structures.**

By DR. A. R. COLLINS (Technical Director, Cement & Concrete Association).—An account of developments in concrete technology since the last symposium.

### **The Early History of Cement in England.**

By P. GOODING (Development Officer, Cement and Concrete Association) and P. E. HALSTEAD (Research & Development Division, Cement & Concrete Association).—The authors give some new facts on the history of the manufacture and early uses of Portland cement, and attempt to resolve some of the matters about which different investigators have varied in their conclusions. The paper includes copies of a number of original documents and patents.

### **Thermodynamics of the Cement Kiln.**

By H. GYGI, in collaboration with F. GUYE (Holderbank-Wildeggen Cement Works, Switzerland).—By setting up a heat balance an attempt is made to show how much of the supplied heat is used as effective heat and how much is lost. The process in the kiln is analysed with regard to the structural changes in the raw material, the respective temperatures, and the flow of the gases. A new type of heat exchanger, equally suitable for the kiln and cooler, is described. The axial velocity of the transport of material through the kiln is determined as well as the relations between speed, inclination, and diameter as a function of the ratio of material in a kiln section, for which an optimum is given. A method is described for calculating the dimensions of a rotary kiln.

### **Oil Well Cements.**

By W. C. HANSEN (Universal Atlas Cement Co., U.S.A.).—Portland cements are used by the petroleum industry for the cementing of gas and oil wells at temperatures ranging from atmospheric to about 350 deg. F. and at pressures ranging from atmospheric to about 18,000 lb. per square inch. Slurries of such cements must remain pumpable at these elevated temperatures and pressures for periods up to about four hours, and should then harden fairly rapidly. The paper outlines the operations of drilling and cementing wells and reviews the production of cements for this purpose and the methods of testing such cements at high temperatures and pressures. The paper also describes certain special

cements and presents data on the influence of pressure upon the strengths and heats of hydration of cement pastes cured at elevated temperatures.

### **The Influence of the Fineness of Cement Raw Mixtures on their Burnability.**

By T. HEILMANN (F. L. Smidth & Co. A./S., Copenhagen).—The object of the tests was to find what fineness of raw mixture is economically justifiable in order to ensure satisfactory burnability. The tests were made by burning nodules of 12 mm. diameter in such a way that the dried nodules were first calcined for half an hour at 950 deg. C. and then transferred directly to the kiln for the final burning, where they were burnt, generally for 20 minutes, at varying temperatures. The temperature necessary to obtain clinker with a suitably low content of free CaO was then investigated. A description is given of tests on two standard raw mixtures, which show among other things the effect of the burning time on the temperature required.

Further tests were made on nodules of different sizes. These tests show that variation of the nodule size up to 25 mm. diameter has no appreciable influence on the burning results, whereas larger nodules called for a longer burning time or a higher temperature. Next tests were made to determine the influence of the content in the raw mixture of coarse silica and calcite particles, that is particles above 0.09 mm. The tests showed that a mixture with a comparatively high lime-saturation factor (LSF 95 per cent.) should not contain more than 0.5 per cent. of coarse silica above 0.2 mm. With a lower lime-saturation factor somewhat larger amounts of coarse silica are permissible, but then the burnability will suffer to some degree. During the burning, the coarse silica is converted into soluble silicates, mainly dicalcium silicate, but without any tricalcium silicate. If the coarse limestone particles are pure calcite, up to 5 per cent. limestone particles above 0.15 mm. are permissible. If the limestone particles contain impurities consisting of siliceous minerals, a considerably larger amount of coarse limestone particles is permissible.

Research has also been made on the importance of the distribution in the mixture of particles below 0.07 mm. These tests proved that minor changes in the distribution of the fine particles have no notable influence on the burnability of the mixture. A certain amount of very fine particles, about 35 per cent. below 15 microns, seems to be necessary in order to give a reasonable burnability. This amount will, however, always be present in straight-ground as well as in closed-circuit-ground mixtures prepared from hard materials. The considerable increase in the amount of fine particles which occurs when washable materials are used causes an improvement in the burnability.

### **Interstitial Phases in Portland Cement Clinker.**

By HERBERT INSLEY (National Bureau of Standards, U.S.A.).—The interstitial phases including glass, crystalline "dark" and "light" material, free MgO and free CaO, are briefly reviewed. The variable properties of the interstitial liquid at clinkering temperatures, especially composition and viscosity, partly determine

the degree of crystallinity and the nature of the crystals in the resulting product after cooling. The diffraction pattern which has been attributed to glass in clinker is more probably that of a metastable ferrite similar to tricalcium aluminate. Although the nature of the prismatic dark interstitial material has not been established it may be assumed to be a form of tricalcium aluminate, unknown in the pure state, stabilised by compounds of alkalis in solid solution. The deepened pleochroism of the crystalline interstitial ferrite phase in the presence of MgO may be caused by the displacement of the composition towards the high-iron end of the solid solution series,  $2\text{CaO} \cdot \text{Fe}_2\text{O}_3 \cdot 6\text{CaO} \cdot 2\text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ . The crystallisation of interstitial magnesia is strongly influenced by the rate of cooling of the clinker through the range of crystallisation. The crystallinity and texture of the clinker are probably greatly affected by the properties of the interstitial material during the cooling period. Little is known quantitatively of these characteristics. Especially needed are data on viscosities of interstitial liquid, equilibrium relations of the calcium aluminates, and a fresh study of the system  $\text{CaO-MgO-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$ .

### The Tricalcium Silicate Phase.

By J. W. JEFFERY (Birkbeck College, London University).—Evidence of the existence of an alite phase distinct from pure  $\text{C}_3\text{S}$  is summarised under the headings: powder X-ray investigations; single crystal X-ray investigations; thermal analysis; optical investigations. It is concluded that there can be no longer any reasonable doubt that the alite phase of Portland cement clinker is tricalcium silicate modified by slight "solid solution". A discussion of the literature is followed by a summary of the polymorphism of tricalcium silicate at room temperatures. All the forms so far investigated are strongly pseudo-trigonal with the same cell dimensions, namely,  $a = 7.0$ ,  $c = 25.0$  Å, and space group  $\text{R}\bar{3}\text{m}$ . Alite gives single lines on powder photographs at  $d = 1.46$ ,  $1.48$ , and  $1.76$  Å, while pure  $\text{C}_3\text{S}$  has corresponding doublets or triplets in each case.

The pseudo-structure of  $\text{C}_3\text{S}$  as worked out by the author, and a different arrangement arrived at by O'Daniel and Hellner in a preliminary determination, are described and discussed. For alite the author finds the true cell has  $a = 33.08$ ,  $b = 7.07$ ,  $c = 18.56$  Å,  $\beta = 94^\circ 10'$ , and the space group is  $\text{Cm}$ . The high temperature polymorphism of  $\text{C}_3\text{S}$  is discussed. It is shown that strength development in preparations of alite and pure  $\text{C}_3\text{S}$  in conditions similar to those of normal Portland cement are not significantly different. Finally, the effect of the "solid solution" in alite on the calculated compound composition of clinker is discussed and related to the discrepancies between microscopically observed and calculated compositions.

### The Physical Structure of Cement Products and its Effect on Durability.

By F. E. JONES (Building Research Station).—The paper comprises mainly a review of some of the literature. The properties and structure of cement paste and of aggregates are considered, followed by a discussion of the factors leading to failure of concrete arising from causes inherent in the structure and composition,

excluding external chemical attack other than atmospheric corrosion. A summary is given of the work of Powers and Brownyard on the physical properties of hardened Portland cement paste at about 70 deg. F.

The properties of aggregates are considered with special reference to the coefficients of thermal expansion; other properties of thermal diffusivity, strength, porosity, surface texture and shape are also treated. Consideration is given to methods of measurement of several of the properties mentioned. Much of the paper is devoted to a discussion of the effect on durability of mortars and concretes of improper design and preparation, moisture movements on wetting and drying, thermal movements on heating and cooling, atmospheric corrosion and frost.

### The Reactions of Cement Hydration at Elevated Temperatures.

By GEORGE L. KALOUSEK (University of Toledo, U.S.A.).—The hardening of concrete products at elevated temperatures may be attributed in part to reactions involving the cement and fine aggregate or added silica. These products of reaction may differ widely from those of cement pastes alone. Menzel's relation between strength and raw mixture compositions for autoclaved cement-silica solids was studied by differential thermal analysis (DTA) in terms of reaction solids. The low strengths of cement pastes without or with additions of silica up to 8 to 12 per cent. were indicated to be due in part to the presence of  $\text{Ca}(\text{OH})_2$  and the " $\text{C}_2\text{SH}$ " alpha-hydrate which may function merely as aggregates. As the amounts of added silica were increased, the  $\text{Ca}(\text{OH})_2$  first, and then the alpha-hydrate, reacted to form another reaction product characterized by an exothermic reaction at about 840 deg. to 850 deg. C. This solid may have a composition of about 1.25 C:S.\* As the amount of this phase increased the alpha-hydrate diminished in amount. When the latter phase was exhausted the 1.25 C:S product in turn reacted with the added silica to give products in composition downwards to about 0.9 C:S. The highest strengths among all compositions were observed for the 0.9 to 1.25 C:S compositions.

Autoclaved cement pastes without any silica addition consisted of an amorphous-appearing solid, " $\text{C}_2\text{SH}$ " alpha-hydrate and  $\text{Ca}(\text{OH})_2$ . Hydrothermally synthesised lime-rich gel-like phase in the ternary system differed from the analogous phase prepared at room temperature, and appeared to be the precursor of the alpha-hydrate. The amorphous-appearing solid in autoclaved cement may contain the other cement constituents integrally bound and probably differs from that prepared in the ternary system. The only lime-rich crystalline phase that may be expected to form in autoclaved cement products at the usual processing conditions is the so-called " $\text{C}_2\text{SH}$ " alpha-hydrate. This phase has a composition of 1.8 to 2.4  $\text{CaO}:\text{1.00 SiO}_2:\text{1.00 to 1.25 H}_2\text{O}$ .

Previous and new data indicate that the  $\text{C}_3\text{AH}_6$  solid solution or the related hydrogarnets do not appear as hydration products in concrete products processed at elevated or ordinary temperatures. The sulphoaluminates and sulphoterrites of calcium may form for only relatively short periods of time in hydrating cements at temperatures up to about 100 deg. C. At 100 deg. C. these phases could not be

\*C:S is the abbreviated form for mols of CaO per mol of  $\text{SiO}_2$ .

stabilised even with large amounts of gypsum although at temperatures of 90 deg. C. and lower such stabilisation was effected.

Autoclaved  $\text{Ca(OH)}_2$ -free products of lime or cement and pumice and shale, depending on the amount of available silica, may show compositions ranging from about 2.4 to 0.9 C:S. The alpha-hydrate may appear only in samples of the highest C:S ratios but is less likely to form than in cement-silica products. The course of reaction of the products with added silica was similar to that of the cement-silica mixtures. The DTA curves of reaction solids showed that the exothermic peak was rounded and occurred at higher temperatures of 850 deg. to 880 deg. C. for the pumice products, and at 900 deg. to 1,000 deg. C. for the shale products. The higher temperatures of this peak were observed for the lime-rich solids.

Several considerations, such as apparent homogeneity of phase and DTA curves, suggest that the reaction product consists of all the oxide constituents of the ingredients integrally bound. The open structure of the hydrous calcium silicate may possibly accommodate the constituents extraneous to the ternary system lime-silica-water. It is considered that these are the types of solids, of variable compositions, that form in sand-lime bricks and autoclaved concrete products.

### Slag Cements.

By F. KEIL (Forschungsinstitut der Zementindustrie, Germany).—Distinction can be made between three different types of slag cements, namely, Portland slag-cement, slag-Portland cement, and slag-sulphate cement, the first-named component being in each case the principal one. The hydraulic properties of the granulated blastfurnace slag can be established by test. These properties are closely related to the chemical composition of the slags, the relationship being approximately defined by formulæ. Blastfurnace slags with an alumina content of at least 12 per cent. are suitable for the production of slag-sulphate cement. A high addition of calcium sulphate is required and a simultaneous, but not too vigorous, activation by lime or clinker is also necessary. In the decomposition of slags with amine and ammonium salts, distinct differences are shown between the behaviour of slags poor and rich in alumina. It is shown that the content of granulated blastfurnace slag in a slag cement can be determined, even if the distribution in the fraction 0.06 to 0.09 mm. suitable for the required determination is not the same as in the cement.

### Expansive Cements.

By H. LAFUMA (Centre d'Etudes et de Recherches de l'Industrie des Liants Hydrauliques, Paris).—The first satisfactory solution for industrial purposes was found by Hendrickx, and activities in this sphere have been stimulated by Lossier. The necessity of obtaining a controllable expansion that will remain constant with time practically enforces the use of Candlot's salt as the expansion agent; it is made from a sulpho-aluminate clinker obtained by burning a mixture of gypsum, bauxite and carbonate of lime. Expansive cement is prepared from a ternary mixture comprising Portland cement, which imparts its particular

properties to the final product; sulpho-aluminate clinker, which is the expansion agent; and blastfurnace slag, the stabilising agent, the slow action of which enables the expansion to take place besides absorbing the excess of sulphate of lime. The composition of these constituents, their relative proportions, and their fineness are the principal factors which influence the expansion.

### The Ferrite Phase.

By G. L. MALQUORI (Istituto di Chimica Industriale dell' Università di Napoli) and V. CIRILLI (Istituto di Chimica Applicata del Politecnico di Torino).—In the first part the anhydrous ferrite phase is dealt with and special attention paid to the binary system  $\text{CaO-Fe}_2\text{O}_3$ , because this is fundamental to the tracing of the phase diagram of the ternary system  $\text{CaO-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$ , which cannot yet be considered as finally completed. It has been ascertained that only two calcium ferrites exist, namely, the mono- and the dicalcium ferrite. The phase diagram, however, as plotted by Sosman and Merwin, cannot be considered as completely satisfactory. Dicalcium ferrite has been shown to form a eutectic with calcium oxide; also, the eutectic between monocalcium ferrite and ferric oxide is likely to be nearer to ferrite than has been admitted hitherto. Direct experimental measurements have shown that as soon as the melting process begins the oxygen pressure of the system becomes very high in the region of compositions richer in ferric oxide than monocalcium ferrite. X-ray, as well as microscopical observations, show that it is probable that formation of solid solutions takes place between the monocalcium ferrite and magnetite.

In the ternary system  $\text{CaO-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$  what Yamauchi and Swayze have observed regarding the possibility of the formation of homogeneous solids richer in alumina than brownmillerite must be assumed to be confirmed. Brownmillerite must therefore be considered as an intermediate term in the solid solution series of composition  $2\text{CaO}(\text{FeAlO}_3)_2$ .

Attention should be paid to the fact that it is impossible to obtain homogeneous solids containing less than 20 to 21 per cent. by weight of  $\text{Fe}_2\text{O}_3$ . Such a composition differs slightly from that indicated by Swayze. Present knowledge regarding the zone of the system which is poor in lime must be considered insufficient even for an approximate delineation of that portion of the system. As for hydrated calcium ferrites, the possibility of the formation of a tetra-calcium ferrite, hexagonal in habit, as well as of a cubic tricalcium ferrite can be accepted as fully established. The existence of less basic ferrites, although they cannot be safely excluded, has not so far been supported by sufficient experimental evidence.

### The Alkali Phases in Portland Cement Clinker.

By TERRY F. NEWKIRK (National Bureau of Standards, U.S.A.).—A review is given of previous work on the alkali-clinker systems and of the various forms in which  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  may occur in Portland cement clinker. The importance of the formation of the alkali phases as they affect the burning of cement mixtures and the constitution of clinker is discussed. During burning the alkalis react



preferentially with the available  $\text{SO}_3$  to form alkali sulphates. Alkalis in excess of the molar equivalent of  $\text{SO}_3$  react with the major clinker components to form  $\text{NC}_8\text{A}_3$  or  $\text{KC}_{23}\text{S}_{12}$ . The latter reactions alter considerably the potential compound composition of the clinker and may have a significant effect on the properties of the cement. For certain compositions, the reactions of the alkalis may cause the formation of free  $\text{CaO}$  as an equilibrium product. Equations which take into account the formation of the alkali phases are presented for use in computing the potential compound composition of clinker-type mixtures.

#### The Dicalcium Silicate Phase.

By R. W. NURSE (Building Research Station).—The chemistry and crystal structure of the known forms of  $\text{C}_2\text{S}$  are discussed. The theory of stabilisation of high temperature forms is developed and is shown to account for the complicated phenomena associated with  $\text{C}_2\text{S}$  in slags, cements, and refractories. It is concluded that only  $\beta\text{-C}_2\text{S}$  is likely to occur in Portland cement, but that its rate of hydration will vary according to the type and amount of stabilising agent it contains.

#### Tricalcium Aluminate.

By FRED ORDWAY (National Bureau of Standards, U.S.A.).—Previous investigations of the structure of tricalcium aluminate are reviewed. An apparatus is described which has proved convenient for growing small single crystals of the compound. The status of the current structure determination by X-ray diffraction is indicated, and the approximate structure proposed by Büssem in the Stockholm symposium is discussed in terms of the general principles governing the structure of minerals.

#### The Constitution of Aluminous Cement.

By T. W. PARKER (Building Research Station).—The present state of knowledge of the constitution of high-alumina cement is reviewed and a summary given of the results of a recent investigation at the Building Research Station concerned mainly with the composition of the mineral known as "unstable  $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ " and with the composition of the ferrites occurring in high-alumina cement.

Investigations on the system  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-MgO}$  show that a compound  $6\text{CaO} \cdot 4\text{Al}_2\text{O}_3 \cdot \text{MgO} \cdot \text{SiO}_2$  occurs as a primary phase. The pure compound, which melts incongruently, is isomorphous with the "unstable  $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ " mineral of high-alumina cement and it is inferred that the composition of the latter is  $6\text{CaO} \cdot 4\text{Al}_2\text{O}_3 \cdot \text{FeO} \cdot \text{SiO}_2$ .

Investigations of the ferrites in polished sections under the microscope by reflected light made use of a new microreflectivity method. The ferrites present correspond to compositions on the line  $6\text{CaO} \cdot 2\text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3 - 2\text{CaO} \cdot \text{Fe}_2\text{O}_3$ . The ferrites in cements containing mainly "unstable  $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ " are at the  $6\text{CaO} \cdot 2\text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$  end of the solid solution series; those in cements containing mainly  $\text{CaO} \cdot \text{Al}_2\text{O}_3$  are in the range of compositions of molecular proportions between  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$  and  $6\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{Fe}_2\text{O}_3$ . No new evidence was obtained which would indicate whether any of these three ferrite compositions are true



compounds. It is confirmed that  $\text{FeO}$  can appear as a final crystallisation phase, and possible assemblies of compounds which can occur are indicated.

These data are used to devise a method of calculation of compound contents, based on the analysis of the cement and an additional analysis of the residue insoluble in acid. The results have been compared with qualitative observations under the microscope and also with some limited quantitative microscope measurements. Except in one case the agreement is reasonably good, bearing in mind the approximations and assumptions which had to be made.

The data available are even less adequate to enable a method of formulation of raw mixtures to be indicated than to calculate the compound composition when the cement is made. However, a possible direction of formulation is developed which shows fair agreement with practice in cements made in the laboratory.

Some observations on the relation of constitution to setting time are reported. It is shown that the presence of  $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$  leads to fast setting. Data are also given on the effect on hydration of the presence of alkalis which accelerate the set. The effect of a number of other additions is also reported. Borax, boric acid, and tartaric acid delay the set to an extent likely to be deleterious. Increased fineness of grinding of the cement tends to shorten the setting time; aeration and limited prehydration in the grinding mills tend in the reverse direction.

Some observations are given on the possibilities of further investigation. A study of the equilibrium of the iron oxides and oxygen under the furnace conditions of aluminous cement manufacture is amongst the most important of the outstanding items. A series of phase equilibrium studies is also indicated. Finally it is suggested that preliminary study of the relation between, say, strength and compound composition would be worth while as a guide to the practical value of further studies.

### **The Reactions and Thermochemistry of Cement Hydration at Ordinary Temperature.**

By HAROLD H. STEINOUR (Portland Cement Association, U.S.A.).—The evidence available for establishing the products of Portland cement hydration is mainly indirect. It consists largely of studies made on the simpler systems  $\text{CaO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$ ,  $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ , and  $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot \text{H}_2\text{O}$ . Alkalis and  $\text{Fe}_2\text{O}_3$  have been included in other limited studies.

Determinations of heat of hydration of Portland cement paste have been made mainly for practical purposes, but comparison of the data with values for the clinker compounds hydrating separately has afforded some indication of the chemistry of the matter. Recent studies have provided data on heat evolution over  $6\frac{1}{2}$  years. Other studies have given new data on the effect of the water: cement ratio. Continuous records of the heat evolution of cement paste during the setting period, and during the first few days, have furnished indications of the early course of the cement reactions.

Independent reaction of the major clinker compounds is capable in large measure of accounting for the rates and ultimate values of the hydration, strength

development, and heat evolution of cement paste, but this does not rule out the possibility of some interaction. Free calcium hydroxide is produced, and the liquid phase is saturated with this compound. The other products formed in cement paste are gel-like and very difficult to identify by microscopy or X-ray analysis. A promising new method of approach is that of differential thermal analysis.

It appears probable that the high-sulphate calcium sulpho-aluminate is formed, but then reacts with more of the calcium aluminate to form a solid solution of lower sulphate content. Some tetracalcium aluminate hydrate may form, as a non-equilibrium product, after the gypsum has all reacted. The calcium silicates evidently form hydrated calcium silicate that is perhaps lime absorptive and has an overall lime:silica ratio in the neighbourhood of 2 or less, the precise value being uncertain. Iron oxide may perhaps partially substitute for alumina in the reaction products.

#### **Development of Cements for Special Uses in the United States.**

By MYRON A. SWAYZE (Lone Star Cement Corporation, U.S.A.).—The paper presents an account of the methods by which special cements are evolved by co-operation between cement users and manufacturers in the United States. The history of the development of the five A.S.T.M. cement specifications is outlined. Cements meeting the A.S.T.M. specifications have been found unsatisfactory in certain special applications, and the reasons for the autoclave expansion test and the recently introduced alkali content limitation are explained. The future of masonry, pozzolanic, and air-entraining cements is considered, and brief mention is made of the development of such specialised products as oil well cements.

#### **Chemical Aspects of the Durability of Cement Products.**

By T. THORVALDSON (University of Saskatchewan, Canada).—After a brief account of the search for a cement of the Portland cement type resistant to the chemical action of natural waters, especially those containing sulphates, experimental data is presented for the expansion and changes in tensile strength of lean mortars, made of A.S.T.M. type I and V cements, exposed to sulphate solutions. The available evidence on the effect of the chemical compounds which may be present in Portland cement on the sulphate resistance of mortars and concrete is summarised as well as the influence of additions of pozzolanic materials. Some theories of the nature of sulphate resistance are considered.

#### **Masonry Cement.**

By CHARLES E. WUERPEL (Marquette Cement Manufacturing Co., U.S.A.).—Masonry cement in the U.S.A. is passing through a period of development which appears to be proceeding towards increased uniformity in constitution and predictability of performance. The preponderant constituent is a very finely interground homogeneous mixture of Portland cement and limestone given a very high degree of plasticity and water retention by the interground addition

of an air-entraining agent, and regulated in setting time by gypsum. Specifications are very loose in their requirements. In order that masonry cement may acquire prestige similar to that of Portland cement, the following additions to and improvements in the existing specifications must be made: (a) Autoclave test for soundness with a maximum permissible expansion of the order specified for Portland cement; (b) Workability retention test to ensure adequate retention of plasticity; (c) Plasticity index to ensure high order of plasticity; (d) Air content minimum limit, as a transitory step during development of adequate criteria for (c), since "plasticity" seems to be very largely a direct function of air content; (e) Compressive strength criteria should be maintained, but less emphasised in importance; (f) Bond tests do not appear feasible at present; (g) Requirement for uniform unit weight; preferably 70 lb. per bag and with each bag understood to contain 1 cu. ft. (loose volume) of cement. With greatly increased awareness of the importance of improvements in this type of cement, there is greatly intensified research. Major progress towards uniform high quality and increased usefulness of masonry cement seems assured.

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#### **Effect of Fineness of Raw Materials for Cement.**

At the last annual convention of the Japanese Cement Engineering Association some research carried out by the Ube Kosan Co., Ltd., on the properties of finished cement of the size of the raw materials was described.

It was found that, even if the raw mixes have the same specific surface area, when the individual elements (limestone and clay) have different surface areas and the clinkers have different contents of free lime minerals, the resulting cements have different strengths. It is recommended that for most favourable results the ratio of the specific surface area of clay to limestone should be 1.00 for low-lime cement and 1.40 for high-lime cement.

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#### **Cement Works at Ceylon.**

MESSRS. Mirrlees, Bickerton & Day, Ltd., inform us that in their advertisement in the September number of this journal they inadvertently referred to the alternators coupled to their engines at the Kankasanturai, Ceylon, Cement Works as being of Brush manufacture, whereas they were manufactured by Messrs. Crompton Parkinson, Ltd., as stated on page xiii of the same number.

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#### **A New Cement Factory in Paraguay.**

A NEW cement factory at Valle Mi, Paraguay, has recently started production. The capacity of the factory is 10,000 sacks per week and it is reported that there will be a surplus for export.

## Hydrophobic Cement.

WITH reference to a paragraph in this journal for January, 1952, reporting that a Russian chemist claimed to have invented a hydrophobic cement, the A.S.P. Chemical Co., Ltd., of Gerrards Cross, inform us that a hydrophobic cement, for which a patent application has been made, was produced in their laboratory in August, 1950. This cement was produced in connection with soil stabilisation, and it was found that soil treated with this type of cement was more resistant to absorption of water and could be stored uncovered without deterioration. The initial setting time is 2 hours 50 minutes and the final setting time 3 hours 55 minutes.

Absorption tests were made on prisms, 3 in. by 3 in. by 6 in., made of standard sand and ordinary Portland cement, and standard sand and hydrophobic cement which, 14 days after casting, were dried, weighed, and stood upright in  $\frac{1}{2}$  in. of water. The absorptions are calculated as percentages of the dry weight, and were: Ordinary Portland cement—1 hour, 0.67; 24 hours, 3.22; 3 days, 4.87; 7 days, 6.06; hydrophobic cement—1 hour, 0.52; 24 hours, 2.63; 3 days, 3.79; 7 days, 4.72.

The moisture-resistant property was tested by spreading hydrophobic cement in a damp cupboard at 90 per cent. relative humidity and 62 deg. F. for seven days and turning it over at intervals. Three 6-in. cubes of 1:2:4 mixture were then made. The average density of three cubes was 143 lb. per cubic foot, and the average compressive strength at seven days 2,390 lb. per square inch. Similar cubes made with ordinary Portland cement as received from the cement works had a density of 147 $\frac{1}{2}$  lb. per cubic foot and a compressive strength of 2,540 lb. per square inch.

It is claimed that this cement is water-resisting so long as it remains static, and that the water-resisting properties are reduced when the cement is agitated with the aggregate in the concrete mixer.

Hydrophobic cement is made by introducing a chemical with the gypsum in the grinding mill, and it is expected that a saving of 20 per cent. of the wear on the mill will be effected.

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### Book Review.

**"Liants Hydrauliques".** By H. Lafuma. (Paris: Dunod. Price 760fr.)

The French standard specifications describe ten different kinds of cements and there are, in addition, others which have not been standardised. While presenting certain advantages this multiplicity of cements necessitates a wide knowledge on the part of the user to enable the best choice of the available cements to be made for any particular purpose. The author describes the constituents of the various cements available in France, the theories of setting and hardening, the properties of each type and their suitability for a variety of uses.

## Effect of Sulphur in Clinker.

A PAPER on the effect of sulphur on the alkali compounds of Portland cement clinker, by Mr. Terry F. Newkirk, is given in the "Journal of Research of the United States National Bureau of Standards" for November, 1951. This investigation shows that the compound  $\text{Na}_2\text{O} \cdot 0.8\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ , which is known to be one of the forms in which  $\text{Na}_2\text{O}$  may occur in Portland cement clinker, is unstable at clinkering temperatures in the presence of  $\text{SO}_3$ . This compound reacts with  $\text{SO}_3$  to form  $\text{Na}_2\text{SO}_4$  and  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ . Any excess of  $\text{Na}_2\text{O}$  will remain as  $\text{Na}_2\text{O} \cdot 0.8\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ , become a constituent of the clinker glass, or enter into solid solution with one of the other clinker components. In clinker compositions containing both soda and potash together with  $\text{SO}_3$ , an alkali-sulphate phase is produced that contains both of the alkalis. For molecular ratios  $\text{R}_2\text{O}/\text{SO}_3$  greater than unity, a preferential reaction of the  $\text{SO}_3$  with  $\text{K}_2\text{O}$  is indicated. Empirical relationships between the alkalis and the  $\text{SO}_3$  of the cement mixture indicate that the alkalis first combine with the  $\text{SO}_3$  in the approximate molecular ratio  $\text{K}_2\text{O}/\text{Na}_2\text{O} = 3$  to the extent that the composition limits of the mixture permit. The composition of the alkali-sulphate phase for mixtures of varying soda-potash contents with  $\text{R}_2\text{O}/\text{SO}_3$  molecular ratios equal to 1, 2, and 3 have been determined. Equations are developed for calculating the approximate composition of the alkali sulphate and the potential phase composition of clinker-type mixtures having other  $\text{R}_2\text{O}/\text{SO}_3$  ratios.

The author states that Portland cement clinker contains, in addition to the major constituent oxides of calcium, aluminium, and silicon, small quantities of other oxides that occur in the raw materials. The alkalis  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  have a particular interest because of their unfavourable reaction with certain types of aggregate used in concrete, and during the burning process these minor oxides affect the temperature at which the first liquid forms and the nature and quantity of the phases that ultimately constitute the clinker. The nature and quantity of these phases determine, for the most part, the physical and chemical properties of the cement. Small amounts of the alkalis may have an effect on the phase relations in the clinker of a magnitude not commensurate with their low concentration.

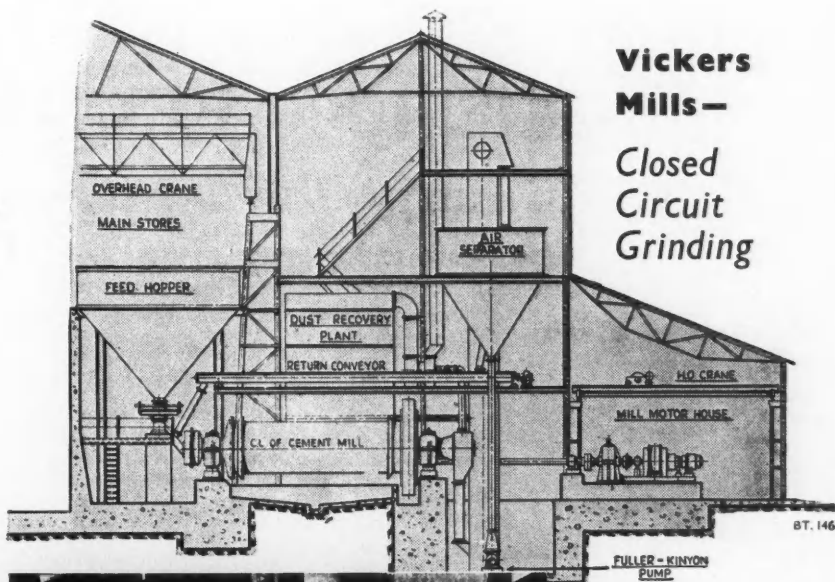
The nature of the alkali-bearing phases has been studied by various investigators with mixtures containing  $\text{CaO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ , and either  $\text{Na}_2\text{O}$  or  $\text{K}_2\text{O}$ . They recognised, however, that acidic oxides such as  $\text{SO}_3$  and  $\text{TiO}_2$ , when present, may react with the alkalis during the burning process to produce new phases. One investigator, Mr. W. C. Taylor, found that, for mixtures approximating Portland cement compositions and composed of  $\text{K}_2\text{O}$ ,  $\text{CaO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{MgO}$ , the stable compound of potash is  $\text{K}_2\text{O} \cdot 23\text{CaO} \cdot 12\text{SiO}_2$ . He reported, however, that this compound is unstable when heated in the presence of  $\text{SO}_3$ , the reaction being represented by the equation  $\text{K}_2\text{O} \cdot 23\text{CaO} \cdot 12\text{SiO}_2 + \text{CaSO}_4 = 12(2\text{CaO} \cdot \text{SiO}_2) + \text{K}_2\text{SO}_4$ . He found molten potassium sulphate to be immiscible with the clinker liquid, to show no tendency to react with the com-

ponents of mixtures containing  $3\text{CaO} \cdot \text{SiO}_2$ ,  $2\text{CaO} \cdot \text{SiO}_2$ ,  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ ,  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ , and  $\text{MgO}$ , and to crystallise readily upon cooling. In 11 out of 19 commercial clinkers subjected to microscopic examination, he found the phase identified as potassium sulphate. In a few subsequent experiments he observed that a solid solution of sodium and potassium sulphates appeared upon heating certain mixtures of  $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{O} \cdot \text{CaO} \cdot \text{SiO}_2$ , and  $2\text{CaO} \cdot \text{SiO}_2$ . As in the case of the potassium compound, he found sodium sulphate to be essentially immiscible with the clinker melt. A phase identified as  $\text{K}_2\text{SO}_4$  occurred in several  $\text{Na}_2\text{O} \cdot \text{K}_2\text{O} \cdot \text{CaO} \cdot \text{SiO}_2 \cdot \text{SO}_3$  mixtures of high  $\text{K}_2\text{O}/\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}/\text{CaO}$  ratios. The manner in which the soda was combined in these mixtures was not determined. Mr. W. R. Eubank made a preliminary investigation of the clinker phases produced upon heating mixtures containing  $\text{Na}_2\text{O}$  and combinations of  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  together with  $\text{SO}_3$ . As a result of microscopic studies of quenched and slowly cooled charges, he found that the compound  $\text{Na}_2\text{O} \cdot 0.8\text{CaO} \cdot 3\text{Al}_2\text{O}_3$  is decomposed by heating with calcium sulphate in the range 1300 deg. C. to 1470 deg. C. Charges containing equimolar quantities of these two compounds were found to consist only of  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$  and  $\text{Na}_2\text{SO}_4$  after heat treatment, indicating complete reaction. The alkali sulphate produced in the reaction was found to be stable in the presence of  $3\text{CaO} \cdot \text{SiO}_2$ ,  $2\text{CaO} \cdot \text{SiO}_2$ ,  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ , and  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ . Indications were obtained that if a solid solution of  $\text{Na}_2\text{O}$  and  $\text{Fe}_2\text{O}_3$  in  $2\text{CaO} \cdot \text{SiO}_2$  was prepared, the  $\text{Na}_2\text{O}$  was not removed from this solution by heating it with  $\text{CaSO}_4$ . Some of the mixtures also contained  $\text{K}_2\text{O}$  either as  $\text{K}_2\text{O} \cdot 23\text{CaO} \cdot 12\text{SiO}_2$  or as  $\text{K}_2\text{SO}_4$  in addition to the soda compounds. Studies of these mixtures were inconclusive, due to the difficulty in distinguishing between certain of the compounds having practically identical optical properties. This made it evident that any further work on this subject would require the application of a different experimental method.

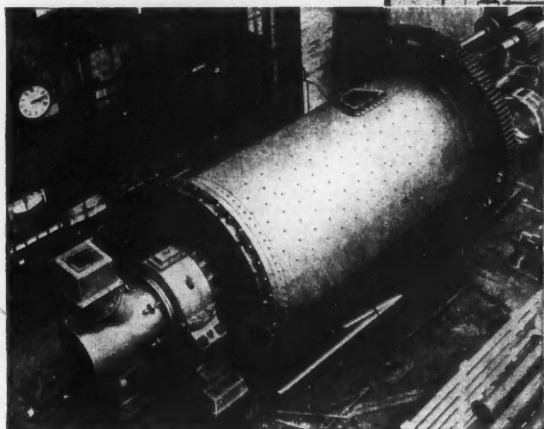
Portland cement clinker ordinarily contains both soda and potash as well as  $\text{SO}_3$ . It was necessary, therefore, to study further the effect of  $\text{SO}_3$  on the alkali compounds of clinker containing both soda and potash. This study has provided a basis for the development of equations for approximating the potential phase composition of Portland cement clinker containing known quantities of  $\text{K}_2\text{O}$ ,  $\text{Na}_2\text{O}$ , and  $\text{SO}_3$ .

In discussing the results of his investigation the author states that it appears from this and earlier studies that when mixtures approximating Portland cement compositions contain  $\text{SO}_3$ , the alkalis in these mixtures will react with the  $\text{SO}_3$  during the burning process to produce an alkali-sulphate phase. The investigation confirms that this alkali-sulphate is immiscible with the primary clinker melt and stable in the presence of the major clinker components.

Cement mixtures containing only  $\text{K}_2\text{O}$  as the alkali, together with  $\text{SO}_3$ , will, after burning, have the available  $\text{SO}_3$  combined with the  $\text{K}_2\text{O}$  as the compound  $\text{K}_2\text{SO}_4$ , which will appear in the form of crystals in the clinker. If more  $\text{K}_2\text{O}$  is present than the quantity required to combine with the available  $\text{SO}_3$ , this  $\text{K}_2\text{O}$  will become a constituent of the clinker glass or, if cooling is sufficiently slow, may appear as the compound  $\text{K}_2\text{O} \cdot 23\text{CaO} \cdot 12\text{SiO}_2$ .



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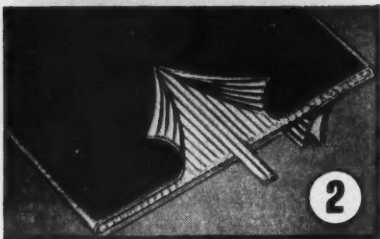


# CONVEYOR AND TRANSMISSION BELTS

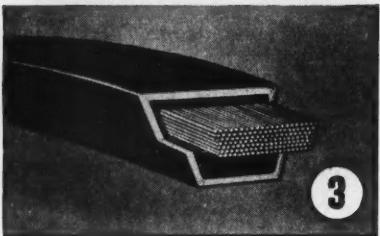
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...and keep on carrying it



1



2



3

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Specifically built for modern high-speed, small-pulley machinery, Goodyear Endless Cord Transmission Belts incorporate a patent *balanced* construction of load-carrying cords. Their H.P. capacity is 33 1/3% greater than ordinary belts of equivalent thickness; they are genuinely endless; and have an unusual degree of flexibility which gives a firm grip on small pulleys at high speeds.

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If a cement mixture contains only  $\text{Na}_2\text{O}$  as the alkali, this oxide will combine with the available  $\text{SO}_3$  to form  $\text{Na}_2\text{SO}_4$ , which will appear as finely divided crystals in the clinker unless cooling has been extremely rapid. Soda in excess of that required to combine with the  $\text{SO}_3$  will become a constituent of the glass or may enter into solid solution with  $2\text{CaO} \cdot \text{SiO}_2$  or one of the other clinker components. If cooling were sufficiently slow, some of the excess soda might appear in the form of the compound  $\text{Na}_2\text{O} \cdot 0.8\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ .

When both the alkalis  $\text{K}_2\text{O}$  and  $\text{Na}_2\text{O}$  are present in cement mixtures together with  $\text{SO}_3$ , they react at clinkering temperatures to form a separate liquid phase, which changes to a single solid solution on cooling. This solid solution is stable above a temperature that varies from 400 deg. C. to 600 deg. C., depending on the sulphate composition. The sulphate phase has a constant composition if both  $\text{Na}_2\text{O} \cdot 0.8\text{CaO} \cdot 3\text{Al}_2\text{O}_3$  and  $\text{K}_2\text{O} \cdot 0.23\text{CaO} \cdot 12\text{SiO}_2$  are present at crystalline equilibrium.

TABLE 1.

A. Mixtures having $\text{R}_2\text{O}/\text{SO}_3$ molecular ratios equal to or less than 1.0	
$3\text{CaO} \cdot \text{SiO}_2$ .....	= 4.0710 CaO - 7.6024 $\text{SiO}_2$ - 6.7187 $\text{Al}_2\text{O}_3$ - 1.4296 $\text{Fe}_2\text{O}_3$ + 3.6826 $\text{Na}_2\text{O}$ + 2.4238 $\text{K}_2\text{O}$ - 2.8516 $\text{SO}_3$
$2\text{CaO} \cdot \text{SiO}_2$ .....	= 8.6024 $\text{SiO}_2$ + 5.0683 $\text{Al}_2\text{O}_3$ + 1.0784 $\text{Fe}_2\text{O}_3$ - 2.7780 $\text{Na}_2\text{O}$ - 1.8284 $\text{K}_2\text{O}$ + 2.1511 $\text{SO}_3$ - 3.0710 CaO
$3\text{CaO} \cdot \text{Al}_2\text{O}_3$ .....	= 2.6504 $\text{Al}_2\text{O}_3$ - 1.6918 $\text{Fe}_2\text{O}_3$
$4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ .....	= 3.0430 $\text{Fe}_2\text{O}_3$
$\text{CaSO}_4$ .....	= 1.7005 $\text{SO}_3$ - 2.1960 $\text{Na}_2\text{O}$ - 1.4453 $\text{K}_2\text{O}$
$\text{Na}_2\text{SO}_4$ .....	= 2.2914 $\text{Na}_2\text{O}$
$\text{K}_2\text{SO}_4$ .....	= 1.8500 $\text{K}_2\text{O}$
B. Mixtures having $\text{R}_2\text{O}/\text{SO}_3$ molecular ratios greater than 1.0	
$3\text{CaO} \cdot \text{SiO}_2$ .....	= 4.0710 CaO - 7.6024 $\text{SiO}_2$ - 1.4296 $\text{Fe}_2\text{O}_3$ - 6.7187 $\text{Al}_2\text{O}_3$ + 2.4238 $\text{K}_2\text{O}$ + 3.6826 $\text{Na}_2\text{O}$ - 2.8516 $\text{SO}_3$
$2\text{CaO} \cdot \text{SiO}_2$ .....	= 8.6024 $\text{SiO}_2$ + 1.0784 $\text{Fe}_2\text{O}_3$ + 5.0683 $\text{Al}_2\text{O}_3$ - 23.769 $\text{K}_2\text{O}$ - 2.7780 $\text{Na}_2\text{O}$ + 2.1511 (12 $K_s$ + 1) $\text{SO}_3$ - 3.0710 CaO
$3\text{CaO} \cdot \text{Al}_2\text{O}_3$ .....	= 2.6504 $\text{Al}_2\text{O}_3$ - 13.075 $\text{Na}_2\text{O}$ + 10.123 (1 - $K_s$ ) $\text{SO}_3$ - 1.6918 $\text{Fe}_2\text{O}_3$
$4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ .....	= 3.0430 $\text{Fe}_2\text{O}_3$
$\text{K}_2\text{O} \cdot 0.23\text{CaO} \cdot 12\text{SiO}_2$ .....	= 22.345 $\text{K}_2\text{O}$ - 26.288 $K_s$ ( $\text{SO}_3$ )
$\text{Na}_2\text{O} \cdot 0.8\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ .....	= 13.170 $\text{Na}_2\text{O}$ - 10.197 (1 - $K_s$ ) $\text{SO}_3$
$\text{K}_2\text{SO}_4$ .....	= 2.1764 $K_s$ ( $\text{SO}_3$ )
$\text{Na}_2\text{SO}_4$ .....	= 1.7743 (1 - $K_s$ ) $\text{SO}_3$

Under these conditions the molecular fraction of  $\text{K}_2\text{SO}_4$  in the sulphate is  $0.75 \pm 0.04$ .

It is evident that the reaction of a portion of each of the alkalis with  $\text{SO}_3$  during the burning of clinker affects the final phase composition of the clinker. The formation of  $\text{K}_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4$  will greatly reduce the potential quantity of  $\text{K}_2\text{O} \cdot 0.23\text{CaO} \cdot 12\text{SiO}_2$  and  $\text{Na}_2\text{O} \cdot 0.8\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ , which would otherwise be formed in the event of complete equilibrium crystallisation. This in turn regulates the quantity of  $3\text{CaO} \cdot \text{SiO}_2$ ,  $2\text{CaO} \cdot \text{SiO}_2$ , and  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$  appearing in the clinker.

Equations that take into account the effect of  $\text{SO}_3$  on the potential phase composition of  $\text{K}_2\text{O} \cdot \text{Na}_2\text{O} \cdot \text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot \text{Fe}_2\text{O}_3 \cdot \text{SO}_3$  mixtures approximating to the composition of Portland cement clinker have been derived in the manner of Mr. Louis A. Dahl. These equations, in the convenient weight percentage form, appear in Table 1. The application of the equations in Table 1 (B) (for those mix-

tures having  $R_2O/SO_3$  molecular ratios greater than 1.0) requires the preliminary calculation of the value of  $K_s$ , the molecular fraction of  $K_2SO_4$  in the sulphate, for the mixture. This numerical value of  $K_s$ , together with the weight percentage of each of the oxides in the clinker, is then substituted in the equations in Table 1 (B). This preliminary calculation is unnecessary if the mixture has an  $R_2O/SO_3$  molecular ratio equal to or less than 1.0, inasmuch as the equations in Table 1 (A) apply directly to this case.

The use of the equations should be of assistance in controlling the composition of the cement and in regulating burning processes to produce clinker of the desired phase composition.

The mixtures that have been the subject of investigation were designed to furnish data on the stability of the alkali compounds  $K_2O.23CaO.12SiO_2$  and  $Na_2O.8CaO.CAl_2O_3$  in the presence of  $SO_3$  and on the equilibrium products resulting from heating mixtures of these components. These mixtures, while not in themselves of Portland cement clinker composition, were composed of the primary components present in commercial clinker. Furthermore, the phases that appeared in the mixtures after equilibrium was attained were among those commonly found in commercial clinker. These factors provide the basis for applying the experimental data.

Other acidic oxides such as  $P_2O_5$  or  $TiO_2$  when present in the clinker may enter into reaction with the alkalis and otherwise alter the phase relations. The potential phase composition given in Table 1 will then be affected. Likewise, the details of the phase relationships in the senary system  $K_2O-Na_2O-CaO-Al_2O_3-SiO_2-Fe_2O_3$  are as yet unknown, but a study of this system is being made. It has been determined on the basis of microscopic examination of quenched charges containing  $Na_2O.8CaO.3Al_2O_3$  and  $K_2O.23CaO.12SiO_2$  that these two compounds are stable when heated together below 1500 deg. C. These compounds have consequently been included in the list of compounds in Table 1 (B). It is recognised, however, that a certain amount of solid solution may occur between them and the others that have been included in the potential phase composition. It is further recognised that changes in Table 1 may be necessitated as a result of the detailed study of pertinent portions of the indicated senary system.

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### The Cement Industry in the Belgian Congo.

THE production of the works at Lubudi of Ciments du Katanga Cimenkat last year was 150,000 tons. A third kiln with an annual capacity of 50,000 tons has been ordered in Belgium and is expected to be in production by the end of the year 1953. This company's new works at Albertville is nearing completion; this works will have a capacity of 45,000 tons a year.

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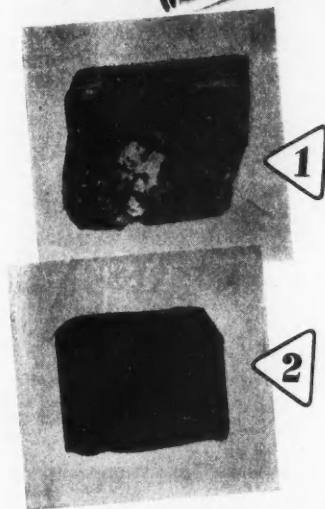
### Cement Production in Japan.

THE production of Portland cement in Japan in the year 1951 was 6,704,000 tons. It is expected that the production will be increased to 7,150,000 tons in 1952 and 7,600,000 tons in 1953.

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## New Cement Factory in India.

THE new cement factory of Orissa Cement, Ltd., at Orissa, India, which started production early in the year 1952, has a capacity of 500 tons per day. The machinery, for production on the wet process, was supplied and installed by Messrs. F. L. Smidth & Co., Ltd.

Limestone is quarried six miles from the factory and is transported by a 2-ft. gauge railway. Clay is available on both sides of the railway, and the factory is conveniently situated near a coalfield. About 800 tons of limestone are transported daily to the factory, where it is tipped into a reinforced concrete hopper from which it is extracted by an inclined conveyor 6 ft. wide and 50 ft. long driven by a variable-speed motor. The conveyor takes the limestone to a 6-ft. by 6-ft. 6-in. hammer crusher which reduces it from about 2 cu. ft. to about 1 cu. in. at the rate of 800 tons per working day. The 1-in. material is transported by an inclined

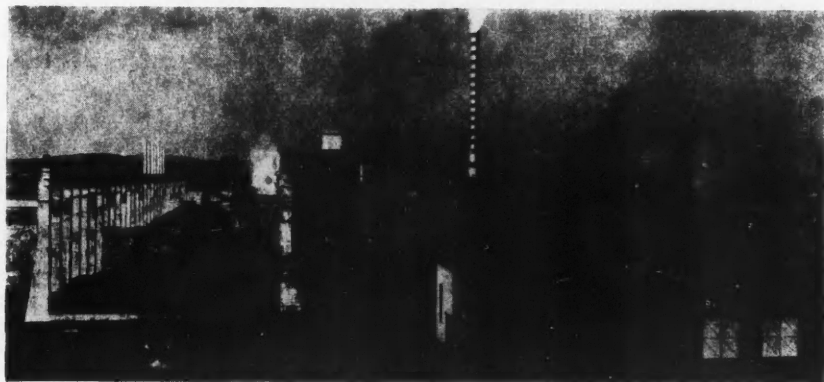


Fig. 1.—The New Cement Factory at Orissa.

rubber-belt conveyor, 32 in. wide and 300 ft. long, to the store, whence it is taken by a horizontal conveyor directly to the raw mill.

The clay slurry from the wash-mill is ground with the crushed limestone in a Unidan mill with a diameter of 8 ft. 6 in. and a length of 40 ft. arranged for central drive through a Symetro gear coupled to a 1,300-h.p. autosynchronous high-tension motor. The slurry is stored in four silos with a total capacity of 175,000 cu. ft. Each silo is fed by an elevator 95 ft. high. From the silos the corrected mixture is drawn into a circular basin where it is mixed by mechanical stirrers and compressed air. From this basin the slurry is supplied to the rotary kiln, which has a total length of 475 ft. The kiln has a diameter of 10 ft. 10 in., increased to 11 ft. 10 in. at the ends. The raw coal is dried and ground in a Tirax air-swept mill, the hot air for which is drawn from the kiln; the mill is also provided with a coal-dust-fired auxiliary furnace which can be used when the coal is very wet. The Unidan cement mill has a diameter of 8 ft. 6 in. and a length of 40 ft. and is

charged with 85 tons of grinding media. This mill is also arranged for a central drive through a Symetro gear coupled to a 1,300-h.p. autosynchronous high-tension motor. The cement is ground in closed circuit. The grinding installation is provided with a six-compartment automatic dust filter. The finished cement is pneumatically pumped into storage silos, whence it is taken by screw conveyors to the packing machines. The cost of the works was about £1,250,000.

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### A 500 ft. Rotary Kiln.

At the Kingsport, Tennessee, U.S.A., works of the Pennsylvania-Dixie Cement Corporation, six 125-ft. dry-process kilns have been replaced by a wet-process kiln 500 ft. long by 12 ft. diameter. This kiln is expected to produce 700 tons of clinker a day with a fuel consumption of 6,000,000 B.T.U.s per ton. The kiln is fired by high-grade bituminous coal. The change to the wet process was largely a result of the stringent local regulations on the emission of dust and of the fact that the local limestone was difficult to grind dry owing to the presence of considerable quantities of clay. Messrs. F. L. Smidth & Co. were the engineers for the conversion of the plant.

The drive of the kiln is claimed to be new to the cement industry. Power is transmitted to the kiln ring-gear through its pinion and gears from a 200-h.p. squirrel-cage motor through a dynamatic water-cooled eddy-current coupling with a speed range of 0 to 1,160 r.p.m. The principle of the dynamatic coupling drive is that a slip is required between the input and output members in order to develop torque, and the torque capacity varies with the difference in speed between the input and output shafts. The input member is driven at a constant speed from the motor and there is no mechanical connection to the output, or driven, member, the transfer of power being effected by the magnetic attraction between the two. A field-coil on the load side is energised by direct-current electricity fed through two slip rings on the output shaft and, by excitation control, the slip is adjusted to meet load requirements. With the motor at "no load" speed, direct current supplied to the field-coil will cause the output shaft to rotate and, through automatic control, the current is readjusted to maintain a desired speed of the output shaft. Direct current for excitation may be supplied from a constant voltage line through a rheostat or potentiometer, or the small amount of direct current required may be available from an electronic control unit fed by alternating current power lines. Automatic speed control is provided through a speed-indicating generator driven by the output shaft which is used in connection with a meter for indicating the speed of rotation of the kiln. Voltage is developed proportional to the driven speed and automatically modulates the control and causes it to supply direct current to the coil to match a load condition.

The unit has individual shafts and bearings for the input and output members. In the case of the kiln drive, the unit is water-cooled to dissipate the heat resulting from the slip-loss. It is claimed that the average slip-loss is about 3 per cent. and



that wind and friction losses are about 2 per cent., indicating a full load efficiency of 95 per cent. The coupling is a simple way to obtain adjustable speed from a constant-speed motor with full-torque starts, and apparently provides accurate speed control over a wide range.

This drive is also applied to the induced-draught fan, the slurry feeder, the dust-return screw-conveyor, the clinker cooler, and the coal feeder to the grinding mill.

The kiln shell is all-welded, both circumferentially and longitudinally, and is supported on six 30-in. tyres of 12 ft. 8 in. inside diameter and 14 ft. outside diameter. The sixth tyre is 14 ft. 4 in. outside diameter with tapered sides for the thrust roller. An oil-lubricated thrust roller mechanism guides the kiln in an axial direction and the slope is  $\frac{1}{2}$  in. per foot. There are 36 stiffener rings for the shell. The shell thickness is  $2\frac{1}{4}$  in. for a length of 7 ft. under each tyre, with a thickness of  $1\frac{1}{4}$  in. for 8 ft. on each side, and the balance is of 1-in. steel plate. The main pinion and secondary gear turn in two bronze bushed oil-lubricated sleeve bearings. The total weight is 2,225,000 lb.

The kiln has a segmented nose-ring of high-heat-resistant cast steel and is fired through a burner pipe of heat-resistant metal insulated with a  $1\frac{1}{4}$ -in. covering of asbestos. It has a heat-resisting stainless steel tip. The burner pipe may later be water-cooled. Heat exchangers at the back-end consist of a single-density pattern of  $\frac{5}{8}$ -in. chain starting 12 ft. from the feed end and extending over a length of 71 ft.; provision has been made to increase this to 86 ft. The present

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length, however, gives excellent nodules of 8 or 9 per cent. moisture at the discharge end. The lining consists of 70 per cent. 6-in. alumina bricks for a distance of 120 ft. in the hot end of the kiln, followed by about 40 ft. of 50 per cent. alumina bricks and, for the remainder and in the chain section, low-temperature firebricks.

The drive is over the third pier and consists of a 200-h.p. squirrel-cage motor through a coupling to the dynamatic coupling, which has its output shaft connected to a double-reduction 32.5 : 1 gear-reducer which in turn is engaged by a coupling to the pinion drive of the master pinion and then the ring gear. A 44-h.p. petrol engine is provided to turn the kiln at  $\frac{1}{8}$  r.p.m. in event of power failure.

This kiln and ancillary plant are described and illustrated in "Rock Products" for January, 1952, from which the foregoing is abstracted.

## Patent Relating to Cement.

### Cellular Concrete.

A concrete or mortar having greater resistance to frost, and increased adhesion to steel reinforcement, and formed with less surface scum, is prepared by adding to the mixture of cement, sand and gravel, and not more than 14 per cent. of water, a plasticizing-agent and a gas-producing substance so that pores of microscopic size are produced and the product contains not more than 8 per cent. of air by volume. The additions may be ground into the cement or added separately or together to the cement or to the gauging-water. The plasticizer acts also as a wetting-agent and so reduces the amount of water required, and may be a cyclic or aliphatic alcohol acid such as tartaric, citric, saccharic, dextronic, or salicylic acid, calcium lignin sulphonate, alizarin sulphonic acid, or humic acid, and may be present in amounts between 0.025 and 0.5 per cent. of the cement. The gas-producing agent is soluble in alkaline liquids and is preferably also a surface tension reducing-agent either alone or as a result of reaction with the alkaline earth metals on the aluminium of the cement and is present in amounts between 0.0005 and 0.5 per cent. of the weight of the cement, sufficient to produce a gas-content of 3 to 8 per cent. by volume. Suitable agents are the alkali-soluble natural or artificial resins, for example, pine resin insoluble in aromatic hydro-carbons, colophony and copal, or casein-, phenol-, or cresol-formaldehyde resins; or soluble sulphonates or sulphates forming alkaline-earth salts, for example, lauryl alcohol sulphonate, fatty acid compounds of sulphonated hydroxyacetic acids, or fatty alcohol sulphonates of cetyl or oil acids; alternatively, metals which react with the solution of the alkaline earths of the binding-agent, for example, calcium, magnesium, aluminium, or their alloys may

be used. Other substances for repelling water, regulating setting, and other purposes, for example, alkali silicates and alkaline-earth chlorides or phosphates may also be included.—No. 634,436 K. Winkler and F. Schenker. July 25, 1946.

Publication of British patents by the Patent Office has been delayed due to the war.

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### INDEX TO VOL. XXV, 1952

	PAGE		PAGE
Africa, A new cement works in North .....	18	Kuhl, H., on Specifications for cements and the trends of development .....	81
Air-entrained cement, Effect of temperature and surface area on .....	104	" " on Fifty years of cement chemistry and manufacture .....	19
Alkali phases in Portland cement clinker, by T. F. Newkirk .....	112	Lafuma, H., on Expansive cements .....	111
Alumina, Aqueous cementitious systems containing lime and, by Harold Steimour .....	13	Levin, Ernest M., Lansing S. Wells, and Walter F. Clarke on The soundness of lime putty .....	77
Aqueous cementitious systems containing lime and alumina, by Harold H. Steimour .....	13	Malquori, G. L., and V. Cirilli on The ferrite phase Mohr, T., H. Togai, and T. Yamanouchi on Blastfurnace slag cement .....	101
Argentina, New cement works in .....	34	Naito, R., on Setting of cement .....	101
<b>AUTHORS:</b>		Newbury, A. D., on Electrical arrangements in modern cement factories abroad .....	85
Adams, M., and G. L. Kalousek on Hydration of cement at medium temperatures .....	17	Newkirk, T. F., on The alkali phases in Portland cement clinker .....	112
Asano, M., T. Yamanouchi, and R. Kondo on Heat of hydration of slag cements .....	103	" " The effect of sulphur in clinker .....	117
Baker, M. C., on Chilanga cement works, Northern Rhodesia .....	63	Nurse, R. W., on The dicalcium silicate phase .....	112
Bernal, J. D., on The structures of cement hydration compounds .....	105	Ohno, Y., on Determination of SO <sub>2</sub> .....	102
Blanks, R. F., and J. L. Gilliland on False set of Portland cement .....	28	Ordway, F., on Tricalcium aluminate .....	112
Bogue, R. H., on The constitution of Portland cement clinker .....	106	Parker, T. W., on The constitution of aluminous cement .....	112
Chujo, K., on Hardness of cement .....	103	Schwalbe, F. G., on A new vertical lime kiln .....	29
Clarke, Walter F., Ernest M. Levin, and Lansing S. Wells on The soundness of lime putty .....	77	Steimour, Harold H., on Aqueous cementitious systems containing lime and alumina .....	13
Collins, A. R., on Developments in the design and construction of concrete structures .....	106	" " The reactions and thermochemistry of cement hydration at ordinary temperature .....	113
Davis, C. E. S., and H. E. Vivian on The reaction of Portland cement with opal .....	7	Swayze, M. A., on Development of cements for special uses in the United States .....	114
Freysinet, E., on A new view of the setting of cement and the nature of concrete .....	1	Swift, H., on New cement works in Uganda .....	35
Gilliland, J. L., and R. F. Blanks on False set of Portland cement .....	28	Tanaka, N., and K. Watanabe on Effect of chemical composition and fineness on the weathering of cement .....	101
Gooding, P., and P. E. Halstead on The early history of cement in England .....	106	Thorvaldson, T., on Chemical aspects of the durability of cement products .....	114
Gygi, H., and F. Guey on Thermodynamics of the cement kiln .....	106	Togai, H., T. Yamanouchi, and T. Mohr on Blastfurnace slag cement .....	101
Hansen, W. C., on Oil well cements .....	106	Ueda, M., on Burning of cement .....	102
Heilmann, T., on The Influence of the fineness of cement raw mixtures on their burnability .....	107	Vivian, H. E., and C. E. S. Davis on The reaction of Portland cement with opal .....	7
Insley, H., on Interstitial phases in Portland cement clinker .....	108	Watanabe, K., and M. Kajii on Fineness of raw materials and strength of cement .....	101
Jeffrey, J. W., on The tricalcium silicate phase .....	108	Watanabe, K., and N. Tanaka on Effect of chemical composition and fineness on the weathering of cement .....	101
Jones, F. E., on The physical structure of cement products and its effect on durability .....	109	Wells, Lansing S., Walter F. Clarke, and Ernest M. Levin on The soundness of lime putty .....	77
Kajii, M., and K. Watanabe on Fineness of raw materials and strength of cement .....	101	Wuerpel, C. E., on Masonry cement .....	115
Kalousek, G. L., on The reactions of cement hydration at elevated temperatures .....	109	Yamanouchi, T., and K. Kondo, on Composition of slag cements .....	101
" " and M. Adams on Hydration of cement at medium temperatures .....	17	" " R. Kondo, and M. Asano, on Heat of hydration of slag cements .....	103
Kami, Y. Mura, and T. Yoshii on Measuring the degree of burning of clinker .....	31	" " T. Mohr, and H. Togai on Blastfurnace slag cement .....	101
Keil, F., on Slag cements .....	110	Yoshii, T., and Y. Mura Kami on Measuring the degree of burning of clinker .....	31
Kondo, K., and T. Yamanouchi on Composition of slag cements .....	101	Blastfurnace slag cement, by T. Yamanouchi, T. Mohr, and H. Togai .....	101
Kondo, R., M. Asano, and T. Yamanouchi on Heat of hydration of slag cements .....	103	" " slags .....	33
		Brazil, Cement production in .....	100

# INDEX - continued from previous page

	PAGE		PAGE
Burning of cement, by M. Ueda .....	102	Magnesia in Portland cement, Determination of free	18
"    clinker, Measuring the degree of, by		Manufacture, Fifty years of cement chemistry and,	
T. Yoshii and Y. Mura Kani .....	31	by Dr. Hans Kuhl .....	19
Canada, New cements works for .....	103	Masonry cement, by C. E. Wuerpel .....	115
Canadian specifications for Portland cement, Revised	6	Mocambique, New cement works in .....	34
Cellular concrete .....	124	Moisture, Unset cement resistant to .....	8
Cement industry in Great Britain .....	75	Morocco, The cement industry in French .....	100
Census of production of the cement industry in Great		Mortar cube tests, Vibrated .....	56
Britain .....	16	Norway, Cement production in .....	59
Ceylon, Cement works in .....	115	Oil well cements, by W. C. Hansen .....	106
Chemical composition and fineness on the weathering		Opal, The reaction of Portland cement with, by	
of cement, Effect of, by K. Watanabe and N.		H. E. Vivian and C. E. S. Davis .....	7
Tanaka .....	101	Paraguay, Cement works in .....	34
Chemistry and manufacture, Fifty years of cement,			
by Hans Kuhl .....	19	<b>PATENTS RELATING TO CEMENT:</b>	
"    of cement, Symposium on the .....	105	Cellular concrete .....	124
Chilanga cement works, Northern Rhodesia, by		Composition of cement .....	79
M. C. Baker .....	63	Manufacturing process .....	80
Clinker, Effect of sulphur in, by T. F. Newkirk .....	117	Non-shrinking cement .....	79
Interstitial phases in Portland cement, by		Slurry, Composition of .....	80
H. Insley .....	108	Phosphate-bearing raw materials, Proportioning .....	33
"    Measuring the degree of burning of, by		Phosphoric anhydride, Treatment of limestone	
T. Yoshii and Y. Mura Kani .....	31	containing .....	35
"    Studies of the constitution of Portland		Phyllite as a raw material for cement .....	63
cement .....	106	Raw materials and strength of cement, Fineness of,	
"    The alkali phases in Portland cement, by		by K. Watanabe and M. Kajii .....	101
T. F. Newkirk .....	112	"    mixtures on their durability, The influence	
Concrete, A new view of the setting of cement and		the fineness of cement, by T. Heilman .....	107
the nature of, by E. Freyssinet .....	1	Research on cement .....	33
Dicalcium silicate phase, The, by R. W. Nurse .....	112	"    Japanese .....	101
The structure of .....	33	Rhodesia, A new kiln for .....	30
Dominica, Cement production in .....	34	"    Chilanga cement works, Northern, by	
Durability of cement products, Chemical aspects of		M. C. Baker .....	63
the, by T. Thorvaldson .....	114	"    Proposed new cement works in .....	8
"    The physical structure of cement products		Set of Portland cement, False, by R. F. Blanks and	
and its effect on, by F. E. Jones .....	109	J. L. Gilliland .....	28
Electrical arrangements in modern cement factories		Setting of cement, by R. Naito .....	101
abroad, by A. D. Newbury .....	85	"    view of the, by E. Freyssinet .....	1
Expansive cements, by H. Lafuma .....	111	Sieves, A mechanical vibrator for test .....	61
Factory in India, New cement .....	121	"    The use of fine-mesh .....	59
Ferrite phase, The, by G. L. Malquori and V. Cirilli...	111	Slag cements, by F. Kiel .....	111
Fineness on the weathering of cement, Effect of		"    Composition of, by T. Yamanouchi and	
chemical composition and, by K. Watanabe and		N. Kondo .....	101
N. Tanaka .....	101	"    Heat of hydration of, by T.	
Flue gases Analysis of .....	57	Yamanouchi, R. Kondo, and M. Asano .....	103
Fuel plant, A pulverised .....	25	Slags, Blastfurnace .....	33
Gases, Analysis of flue .....	57	SO <sub>3</sub> , Determination of, by Y. Ohno .....	102
Germany, A lime works in .....	90	Specification for Portland cement, A new Israeli	
Great Britain, The cement industry in .....	75	standard .....	84
"    "    "    "    "    Census of		Specifications for cements and the trends of develop-	
production .....	16	ment, by Dr. H. Kuhl .....	81
Haiti, Cement works in .....	18	"    Portland cement, Revised	
Hardness of cement, by K. Chujo .....	103	Canadian .....	6
High-alumina cement, The constitution of, by T. W.		Sulphur in clinker, Effect of, by T. F. Newkirk .....	117
Parker .....	112	Surface area on air-entrained cement, Effect of	
History of cement in England, The early, by F.		temperature and .....	104
Gooding and P. E. Halstead .....	106	Symposium on the chemistry of cement .....	105
Holland, The extension of a cement works in .....	9	Sweden, The cement industry in .....	100
Honduras, Proposed cement works in .....	55	Temperature and surface area on air-entrained	
Hydration at elevated temperatures, The reactions		cement, Effect of .....	104
of cement, by G. L. Kalousek .....	109	Temperatures, Hydration of cement at medium, by	
"    at ordinary temperature, The reactions		G. L. Kalousek and M. Adams .....	17
and thermochemistry of cement, by H. H. Steimour		"    The reactions of cement hydration at	
compounds, The structures of cement, by		elevated, by G. L. Kalousek .....	109
J. D. Bernal .....	105	"    The reactions and thermochemistry	
"    of cement at medium temperatures, by		of cement hydration at ordinary temperature, by	
G. L. Kalousek and M. Adams .....	17	H. H. Steimour .....	113
India, New cement factory in .....	121	Test for workability of lime putty .....	5
Indo-China, The cement industry in .....	103	Tests, Vibrated-mortar cube .....	56
Iraq, Cement factory for .....	34	Tricalcium aluminate, by F. Ordway .....	112
Ireland, Cement supplies in Northern .....	50	"    silicate phase, The, by J. W. Jeffrey .....	108
Israel standard specification for Portland cement,		"    The structure of .....	33
A new .....	84	Turkey, Proposed new cement works in .....	55
Japanese research on cement .....	101	Uganda, New cement works in, by H. Swift .....	35
Jordan, Cement factory for .....	12	Underwater construction, Cement for .....	32
Kiln, A 500ft. rotary .....	122	U.S.A., Cement production in the .....	34
"    A new vertical lime, by F. G. Schwalbe		"    Development of cements for special uses in,	
Thermodynamics of the cement, by H. Gygi		by M. A. Swayze .....	114
and F. Guye .....	106	Venezuela, Cement production in .....	100
Kilns, Motors for rotary .....	78	"    New cement plant for .....	100
Lime and alumina, Aqueous cementitious systems		Vibrator for test sieves, A mechanical .....	61
containing, by Harold H. Steimour .....	13	Weathering of cement, Effect of chemical composition	
"    kiln, A new vertical, by F. G. Schwalbe		and fineness on the, by K. Watanabe and N. Tanaka	101
putty, Test for workability of .....	5		
putty, The soundness of, by Lansing S. Wells,			
Walter F. Clarke, and Ernest M. Levin .....	77		
"    works in Germany .....	60		

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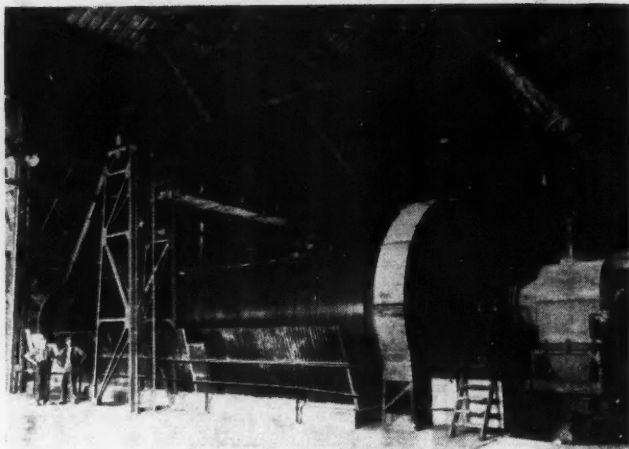
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